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THE DIMETHYL SULPHATE TEST OF CREOSOTE OILS AND CREOSOTE DIPS; A SUBSTITUTE FOR THE SULPHONATION TEST.

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INTRODUCTORY.

In the examination of coal-tar creosote dips, used or offered for use for the official dipping of sheep,¹ the Biochemic Division of the Bureau of Animal Industry has confronted a problem which is commonly set before chemists engaged in the testing of commercial creosote oils, namely, to determine whether any particular sample of oil may be classed as a strictly legitimate coal-tar creosote distilled from gas tar or coke-oven tar, or whether it is probably derived wholly or in part from tars of other origin. The test here to be described has been in use in the laboratories of the Biochemic Division for nearly two years and has been found a helpful aid in arriving at certain data which are generally considered to be of much value in determining the source of origin of creosote oil.

THE SULPHONATION TEST.

The rationale of the sulphonation test has been thoroughly explained and discussed by the Forest Service of this department.² Briefly the process consists in treating a measured amount of a certain "cut" of the oil with hot concentrated sulphuric acid. Aromatic hydrocarbons are thereby sulphonated and the sulphonic acids pass into solution in excess of sulphuric acid, allowing the unattacked paraffin hydrocarbons to rise to the surface as a distinct oily layer of which the volume may be measured in an appropriate apparatus. The proportion of the residue thus isolated is notably different in different classes of creosote oils and so may serve as an aid to their classification.

The theory of the sulphonation test is simple and rational, but its execution, especially in inexperienced hands, is sometimes unsatisfactory and always rather tedious and disagreeable.

¹ Bureau of Animal Industry Order 143, regulation 33.

² Forest Service Circular 112, *The Analysis and Grading of Creosotes.*

THE DIMETHYL SULPHATE TEST.

Some years ago Valenta¹ stated that dimethyl sulphate is miscible with all proportions of aromatic hydrocarbons, while it does not at all dissolve hydrocarbons of the open-chain series, and but slightly dissolves rosin oil. In order, then, to estimate tar oil as an adulterant in petroleum oil or any of its products, or in rosin oil, according to Valenta it was simply necessary to shake thoroughly a measured portion of the oil with a measured portion of dimethyl sulphate in a graduated glass cylinder and to note the resultant increase in volume of the dimethyl sulphate. Valenta cited several experiments on mixtures of various oils to show that the process yielded reliable results.

Valenta's test has been critically examined by Graefe² and by Harrison and Perkin,³ and the following points appear well established:

1. Aromatic hydrocarbons and derivatives thereof are completely soluble in dimethyl sulphate, being miscible in all proportions.
2. Open-chain hydrocarbons show varying degrees of solubility in dimethyl sulphate, ranging from zero to a considerable percentage, light oils as a rule being the more soluble.
3. Treatment of a mixture of aromatic and open-chain hydrocarbons with dimethyl sulphate results in the formation of two layers; the upper contains most of the open-chain hydrocarbons plus a varying but usually small amount of aromatic hydrocarbons retained in solution; the lower layer contains practically all of the dimethyl sulphate, holding in solution most of the aromatic hydrocarbons plus a varying but usually small amount of the open-chain hydrocarbons.

The test therefore is no absolutely quantitative one, as indeed is to be expected from the laws of solubility. Results obtained thereby may, however, under favorable circumstances, closely approach quantitative values, and so may prove very useful for practical work.

APPLICATION OF THE DIMETHYL SULPHATE TEST TO CREOSOTE OILS.

Valenta's object was to determine the amount of tar oils as adulterants in paraffin oils and rosin oils. The purpose of applying the test to creosote oils is the reverse of Valenta's, namely, to determine

¹ Valehtá, E. Ueber die Verwendung von Dimethylsulfat zum Nachweis und zum Bestimmung von Teerölen in Gemischen mit Harzölen und Mineralölen und dessen Verhalten gegen fette Öle, Terpentinöl und Pinolin. *Chemiker-Zeitung*, Jahrgang 30, 1st Semester, p. 266-267. Cöthen, March 28, 1906.

² Graefe, Ed. Ueber die Valenta'sche Reaktion. *Chemische Revue über die Fett- und Harz-Industrie*, Jahrgang 14, Heft 5, p. 112-115. Hamburg, May, 1907.

³ Harrison, T. W., and Perkin, F. M. The action of dimethyl sulphate upon oils of the aromatic and aliphatic series. *Analyst*, vol. 33, no. 382, p. 2-11. London, Jan., 1908.

open-chain hydrocarbons when present in tar oils.¹ The test really lends itself better to the latter purpose, for the aliphatic oils remain behind in tangible form, and so may be directly estimated and readily submitted to further examination.

Since it appears evident from work above referred to that the test will yield the most accurate results when applied to mixtures of heavy oils or oils of high boiling points, the first step in applying it to a creosote oil will be to fractionally distill the oil and apply the test to one of the higher fractions, thus rendering the results comparable to results afforded by the sulphonation test as carried out by the Forest Service. Ordinarily in this laboratory 5 c. c. of the fraction is pipetted into a narrow 25 c. c. burette and shaken with 8 c. c. of dimethyl sulphate after closing the burette with a smooth close-fitting cork. Separation of the residual oil occurs in a short time in the form of a clear, almost colorless, supernatant liquid layer.

The following table illustrates the parallelism between results afforded by the two methods. The distillations were performed from an ordinary fractionating flask with a side tube about halfway up the neck. Temperatures were taken, uncorrected, by a 16-inch thermometer graduated to 360° C.

TABLE 1.—*Comparative residues afforded by sulphonation and dimethyl sulphate tests.*

Kind of oil.	Temperature of fraction.	By sulphonation on 10 c. c.	By dimethyl sulphate per 10 c. c.
Commercial coal-tar creosote so-called "crude carbolic acid, 20 per cent".....	{ 240 to 270 270 to 330	0.2 0.47	c. c. 0.36
Blast-furnace creosote.....	{ 240 to 270 300 to 350	1.60 2.00	2.00 3.20
Oil-gas-tar creosote.....	{ 240 to 270 300 to 350	2.10 2.35	3.70 4.80

Evidently results obtained by the dimethyl sulphate test are parallel with those yielded by the sulphonation test, and though quantitatively differing from the latter, will probably afford data equally as valuable for the purpose of judging the source of origin and the composition of samples of commercial creosote oils. At any rate, until extended experience has shown more fully the range of difference between the results of the two processes the dimethyl sulphate test may serve as a useful "sorting test," leaving the sulphonation test

¹ Although this application of Valenta's test appears sufficiently obvious, yet at the time the manuscript of the present paper was submitted by the writer, several months before publication, the literature on the subject of creosote oils which had come to hand had contained no mention of it. It is now, however, necessary to notice in this connection a paper by Charles N. Forrest, entitled "The characteristics of creosote and tar oils available for wood preservation," appearing in the *Journal of the Society of Chemical Industry*, 1911, vol. 30, p. 193.

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to be employed as a check in the more doubtful or important cases. The test certainly yields quick, clean, and definite results even in wholly inexperienced hands, and requires but a minimum of apparatus and manipulation.

APPLICATION OF THE DIMETHYL SULPHATE TEST TO CREOSOTE DIPS.

Bureau of Animal Industry Order 143 requires that coal-tar creosote dips offered for use in official dipping shall contain rosin soap as the emulsifying agent. Since rosin oil is but partially soluble in dimethyl sulphate, and since highly heated rosin decomposes with the formation of rosin oil, the dimethyl sulphate test can not be applied to the highest distilling fractions of a material containing creosote oil and rosin. To show the effect of rosin upon the amount of residue obtained the following experiments were performed:

Experiment 1.—One part of rosin was dissolved in 3 parts of the commercial coal-tar creosote previously examined with the results noted in Table 1. The material was then fractionally distilled and certain fractions were tested, with the results shown in Table 2.

TABLE 2.—*Tests of fractions from mixture of coal-tar creosote and rosin.*

Temperature of fraction.	Sulphonation residue on 10 c. c.	Dimethyl sulphate residue per 10 c. c.
° C. 240 to 270 270 to 305	c. c. 0.96	c. c. Trace. 2.12

Experiment 2.—A dip prepared from the same creosote, using about 1 part of rosin to 3 parts of oil was fractionally distilled and certain fractions tested, with the following results:

TABLE 3.—*Tests of fractions from distillation of coal-tar creosote dip.*

Temperature of fraction.	Dimethyl sulphate residue per 10 c. c.
° C. 240 to 270 270 to 300	c. c. 0.20 2.52

A comparison of the results afforded by the foregoing experiments with those noted in Table 1 indicates that both the dimethyl sulphate test and the sulphonation test may be consistently applied to mixtures of creosote oil and rosin—that is, to dips—provided the tests are

applied to a fraction distilling between 240° and 270° C., but that neither of the tests is applicable to fractions distilled at a temperature much above 270° C. and approaching 300° C. In practice the test may be combined with the determination of the percentage of water in the dip¹ by providing the distillation flask with a thermometer, using 100 grams of dip, and continuing distillation until a fraction at 240° to 270° C. is obtained. Dimethyl sulphate residues obtained by this method are indicated by Experiment 2 to be somewhat high, hence for more accurate values a method parallel to Experiment 1 is preferable. In such case about 150 grams of dip is well shaken in a separatory funnel with 30 to 40 c. c. of dilute sulphuric acid (1 to 2). After about an hour the lower layer is drawn off as completely as possible, loss of some of the upper layer of course being immaterial. The residual oil is brought into a flask, neutralized with powdered calcium carbonate, and dried by warming with CaCl₂. It is then passed through a folded filter and about 100 c. c. of the material which now contains only oil and rosin is subjected to distillation.

The limitation of the temperatures at which the fraction may be taken evidently allows the recognition of blast-furnace or oil-gas creosote, although the residues obtainable from the lower fractions of such creosotes are notably smaller than those yielded by fractions distilled at a temperature near to or above 300° C. The most serious drawback to the limitation of the temperatures of distillation lies in the fact that it renders entirely possible a failure to detect the admixture with a coal-tar creosote of certain quantities of high-boiling petroleum residues.

If a sample of a coal-tar creosote dip is shaken in a separatory funnel with ether and caustic-potash solution in proper amount a separation into two layers will result. The upper ethereal layer may be washed with potash solution and water, the ether distilled off, and the hydrocarbons present in the dip, now freed from rosin acids and tar acids, will be thus rendered susceptible to thorough examination. The extraction may, of course, be rendered nearly quantitative if desired. The extraction of sufficient oil to allow of fractional distillation will naturally be a somewhat tedious operation and will involve the use of considerable quantities of ether. It seemed desirable, therefore, to determine if the tests might be applied directly to the oil so separated and without previous distillation.

Experiment 3.—Hydrocarbons were extracted from the dip prepared from the sample of commercial coal-tar creosote already described and were tested with dimethyl sulphate with an absolutely

¹ See Bureau of Animal Industry Bulletin 107, "The Analysis of Coal-Tar Creosote and Cresylic Acid Sheep Dips," page 10.

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negative result. To another portion of these hydrocarbons was then added paraffin oil and the mixture tested, with the following results:

TABLE 4.—*Tests on mixtures of paraffin oil with hydrocarbons extracted from dip.*

Nature of mixture.	Sulphona- tion residue on 10 c. c.	Dimethyl sulphate residue per 10 c. c.
Dip hydrocarbons with no addition.....		0.00
2½ volume per cent of paraffin oil.....		.40
5 volume per cent of paraffin oil.....	0.60	.80

Although the hydrocarbons from the dip when treated alone with dimethyl sulphate afforded absolutely no residue, yet the mixtures of paraffin oil and dip hydrocarbons yielded residues considerably greater than the additions of paraffin oil warranted.

The explanation must lie in the fact that the layer of paraffin oil extracted from the dimethyl sulphate layer some of the oils therein dissolved in the first case, possibly nonsaponifiable constituents of rosin, as well as the small amounts of paraffinoid oils indicated by previous tests to be present in the original creosote oil. Hence while the absence of a dimethyl sulphate residue indicates the practical purity of the creosote employed in the preparation of a dip, the method obviously can not be employed for more than approximate estimations of either added foreign creosotes or added petroleum oil.

In practice, then, the examination of a creosote dip will be carried out as follows: Between 20 and 50 grams of dip, depending upon the character and scope of the subsequent examination, is treated with ether and caustic potash solution and the ethereal extract of neutral oils distilled or evaporated to complete removal of ether and moisture.¹ The residue is then examined by the dimethyl sulphate test as previously described. If the result is negative² it is certain that the dip contains neither any large amount of creosote of doubtful origin nor petroleum oils. If the result of the test is positive and further information is desired a sample of the dip may be subjected to distillation in one of the two ways previously described and a test made on the fraction distilling between 240° and 270° C.

¹ Detailed directions for the quantitative separation of coal-tar oils and rosin acids are given in Bureau of Animal Industry Bulletin 107. In the present case the extraction ordinarily need not be quantitative, but it is necessary to free completely the ethereal solution of neutral oils from rosin acids.

² The supernatant layer of oil is sometimes rather dark and may not be easily distinguishable. In such a case it will usually be evident if looked for by reflected instead of transmitted light, or if present in very small amount it may be brought into the narrow neck of the burette just above the stopcock by carefully running out the dimethyl sulphate layer, and is there more readily observed.

CAUTION IN THE USE OF DIMETHYL SULPHATE.

Valenta notes that dimethyl sulphate possesses poisonous properties and hence must be used with a certain amount of care. Lassar-Cohn¹ cites cases of death caused by the material and specifically cautions against allowing it to come in contact with any considerable surface of the skin and against inhaling the vapors. The caution is necessary for the reason that the substance presents an innocuous appearance and its chemical composition would not lead one to expect it to possess particularly poisonous properties. However, employed as here indicated, little danger is to be apprehended, for the quantity used is small, and it is not subjected to heat. Obviously a pipette must never be employed for transference of the substance. Altogether the process appears far less likely to be accompanied by accident than is the sulphonation test, which involves considerable manipulation of comparatively large quantities of hot concentrated sulphuric acid.

Approved.

JAMES WILSON,

Secretary of Agriculture.

WASHINGTON, D. C., May 17, 1911.

¹ Lassar-Cohn. *Arbeitsmethoden für organische-chemische Laboratorien*, vierte Auflage, spezieller Teil, p. 293. Hamburg and Leipzig, 1907.

